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54 **Method for the preparation of titanium-silicalites.**

57 The invention concerns a method for the preparation of titanium-silicalites, in the presence of a templating agent, characterized in that a preformed  $\text{TiO}_2\text{-SiO}_2$  coprecipitate is impregnated with an aqueous solution of said templating agent and in that the thus impregnated material is made to acquire the zeolitic structure of the titanium-silicalites by means of a hydrothermal synthesis.

**EP 0 311 983 A2**

## METHOD FOR THE PREPARATION OF TITANIUM-SILICALITES

The invention concerns a method for the preparation of titanium-silicalites, suited for the catalysis of many an organic synthesis, in particular of the ammoximation in the liquid phase of carbonylic compounds (see European patent 208 311), or the synthesis of propylene oxide (see European patent 200 260).

5 U.S. patent 3 702 886 discloses a new class of aluminosilicates, prepared by hydrothermal (or, by other denomination, "isothermal") synthesis, in the presence of a templating agent, which aluminosilicates are showing a zeolitic structure, nowadays indicated as PENTASIL structure, because of the geometrical shape of the secondary structural units; these aluminosilicates are mainly consisting of ZSM-5 zeolites. More recent catalysts are completely consisting of crystalline silicas (substantially aluminium free), having a  
10 zeolitic structure of the PENTASIL type, similar to the structure of the ZSM-5 zeolites, as disclosed in U.S. patents 4 073 865 and 4 061 724, these particular silicas being indicated with the term "silicalites". Still more recently U.S. patent 4 410 501 discloses a synthetic, crystalline and porous catalytic material, containing titanium, silicon and oxygen in a combined form and having a structure similar to the structure of the silicalite, titanium being present in the structure as a partial substituent for silicon; in said U.S. patent  
15 this kind of material is clearly indicated by the expression "titanium-silicalite" and the same term is reported in a large number of other patents as well (EP 132 550; EP 190 609; EP 208 311; EP 267362).

The preparation of the titanium-silicalites was based, until now, on the initial formation of a gel dispersed in an aqueous solution, followed by a heat treatment in an autoclave under autogenous pressure (hydrothermal synthesis); as the silicon source use was made of a tetra-alkyl-ortho-silicate, of silica in the  
20 colloidal form or of an alkali metal silicate and as the titanium source use was made of hydrolyzable compounds, selected preferably from  $\text{TiCl}_4$ ,  $\text{TiOCl}_2$  and  $\text{Ti}(\text{alkoxy})_4$ . Said preparations required however a high  $\text{H}_2\text{O}:\text{SiO}_2$  ratio, as well as a high (templating agent): $\text{SiO}_2$  ratio and the reactants needed to be heated at a very high temperature for a very long time. The Applicant has now found an alternative, very simple and reliable method, which allows to prepare a titanium-silicalite while lowering in a drastic way the  
25  $\text{H}_2\text{O}:\text{SiO}_2$  ratio and therefore the amount of the reactants, as well as the volume of the apparatuses.

The invention, in its broadest aspect, resides in a method for the preparation of titanium-silicalites, in the presence of a templating agent, characterized in that a  $\text{TiO}_2\text{-SiO}_2$  co-precipitated material, amorphous or having a crystalline structure, containing titanium, silicon and oxygen in a combined form, is impregnated (preferably "dry-impregnated") with an aqueous solution of said templating agent and in that the thus  
30 impregnated material is made to acquire the zeolite structure of the titanium-silicalites by means of a hydrothermal synthesis.

We will now supply some detail concerning the definition of said material. The  $\text{TiO}_2$  coprecipitates, which are also known as " $\text{TiO}_2\text{-SiO}_2$  binary oxides" or as " $\text{TiO}_2\text{-SiO}_2$  mixed oxides" are solid compounds obtained by bringing into contact, under precipitation conditions, at least two solutions (in water and/or in  
35 another solvent) containing soluble compounds of titanium, silicon, and oxygen; the composition and morphologic structure of these compounds may greatly change depending on the reactants concentration, on the solution pH, on the solvent nature and on other co-precipitation conditions. A few examples concerning the preparation of these co-precipitates are recorded on an article of the JOURNAL OF CATALYSIS 35, 225-231 (1974), the content of which is an integrative part of the present disclosure (see  
40 also the plentiful material listed in the references of said article). The possible crystalline structure of said  $\text{TiO}_2\text{-SiO}_2$  co-precipitates, obviously, must be different from the crystalline structure of the derivative, i.e. of the titanium silicalites.

By operating in such a way the hydrothermal synthesis is carried out in the presence of lower amounts of templating agent and at a lower temperature, with respect to the usual methods. The new method allows  
45 to avoid the formation of a gel dispersed in the liquid phase and therefore the synthesis time is lowered in a drastic way; moreover it allows to use, as the silicon and titanium sources, solid  $\text{TiO}_2\text{-SiO}_2$  co-precipitates, which can be easily obtained or can be directly found on the market.

The  $\text{TiO}_2\text{-SiO}_2$  co-precipitates generally show a composition range, expressed as  $\text{SiO}_2:\text{TiO}_2$  molar ratio, from 20 to 200. Excellent results were obtained by using  $\text{TiO}_2\text{-SiO}_2$  commercial co-precipitates, showing a  
50  $\text{SiO}_2\text{-TiO}_2$  molar ratio from 30 to 80. The  $\text{TiO}_2\text{-SiO}_2$  co-precipitates having a high pore volume and a high surface area, for instance a pore volume higher than  $0.5 \text{ cm}^3/\text{g}$  and a surface area higher than  $200 \text{ m}^2/\text{g}$ , proved to be particularly suitable. These co-precipitates are generally available as a powder or in the form of pellets (average size = about 1-3 mm).

When starting from powders, the average size of the obtained titanium-silicalites ranges from 0.2 to 0.5 micrometers.

The  $\text{TiO}_2$ - $\text{SiO}_2$  co-precipitates, preferably dried at  $100$ - $300^\circ\text{C}$ , are impregnated with an aqueous solution of the templating agent; excellent results were obtained by using the dry impregnation technique described for instance by IND. ENG. CHEM. PROD. RES. DEV. 20, 441 (1981), whose content is an integrative part of the present disclosure.

The templating agents, which can give rise to zeolites, silicalites and titanium-silicalites showing a PENTASIL structure, are (as it is known) an awful lot; see for instance: *la Chimica e l'Industria* (Vol. 67 N. 1-2; January-February 1985), the content of which is an integrative part of the present disclosure. We cite, as a mere example and summarily: amines, organic nitro-compounds, alkylene glycols and alkanolamines; use is generally made of tetra-propyl ammonium hydroxide or bromide. The thus impregnated solid is then transferred into an autoclave and it is kept there at  $130$ - $170^\circ\text{C}$  for a time generally ranging from 2 to 20 days, preferably from 3 to 11 days. When the synthesis is over, the solid is rinsed with  $\text{H}_2\text{O}$  till a neutral pH is obtained, afterwards it is dried, for instance at  $120^\circ\text{C}$ , and calcined, for instance at  $430^\circ\text{C}$ . Alternatively, the product may undergo, after drying and before calcination (or after calcination), an "activating" washing, based on hydrogen peroxide, optionally in the presence of an inorganic acid, according to what is described, for instance, by European Patent 267362. The composition of the material to be submitted to the hydrothermal synthesis, expressed as a molar ratio between the reactants, is, as a general rule, as follows:

	generally	preferably
$\text{SiO}_2 : \text{TiO}_2$	20-200	30-80
$\text{OH}^- : \text{SiO}_2$	0.03-0.20	0.05-0.10
$\text{H}_2\text{O} : \text{SiO}_2$	0.1 -10	0.5 -4
$\text{R}_4\text{N}^+ : \text{SiO}_2$	0.03-0.20	0.05-0.10
$\text{R}_4\text{N}^+$ being the organic cation corresponding to the templating agent that was used.		

The X ray diffractometric analysis shows that the obtained compound, according to the new method, is crystalline and is characterized by the typical reflexes of the titanium-silicalite, reported in U.S. patent 4.410.501. In figure 1 a typical diffractogram is reported, obtained according to the process described in Example 1, by using the  $\text{K}\alpha$  radiation of copper. The presence of titanium as a partial substituent for silicon, in the crystalline zeolitic structure, was confirmed by the presence, in the infrared (I.R.) spectrum, of a characteristic absorption band having a maximum substantially at  $950\text{ cm}^{-1}$ . This band, as shown in U.S. patent 4.410.501, does not appear in the I.R. spectrum of the pure silicalite, free from titanium, or in the mechanical mixtures of metal-silicates and of titanium dioxide described by U.S. patent 3.941.871.

In figure 2 an I.R. spectrum is set forth, which is typical of the compound obtained according to the process described in example 1. The measure of the band intensity at  $950\text{ cm}^{-1}$  (on a large number of samples of well crystallized titanium-silicalites, having a different titanium content) allowed to determine the numerical factor to be used for the calculation of the titanium concentration, just starting from the intensity of the band at  $950\text{ cm}^{-1}$ . The determination of the absorption isotherm of nitrogen, according to the known BET method, allowed to ascertain that the volume of the intercrystalline cavities was  $0.170$ - $0.185\text{ cm}^3/\text{g}$ , typical of the crystalline solids having a structure of the PENTASIL type, just as the titanium-silicalites. The titanium-silicalites prepared according to the invention, in which the molar ratio  $\text{Ti}/(\text{Ti} + \text{Si})$  ranges from  $0.0120$  to  $0.0190$ , were successfully used for the ammoximation of carbonylic compounds such as, for instance, acetone, cyclohexanone, methyl-ethyl-ketone (butan-2-one), acetophenone and cyclo-dodecanone, as well as for the oxidation of propylene to propylene oxide.

The ammoximation may be carried out at  $25$ - $100^\circ\text{C}$  (preferably  $30$ - $90^\circ\text{C}$ , in particular  $60$ - $90^\circ\text{C}$ ); tests carried out at  $15^\circ\text{C}$  supplied quite not satisfactory results. The reaction may be carried out at atmospheric pressure or at a pressure slightly higher than the atmospheric, in order to maintain the  $\text{NH}_3$ , in amounts at least equal to the synthesis requirement, dissolved in the reaction medium. The molar ratio  $\text{H}_2\text{O}_2$ : carbonylic compound may generally range from  $0.3$  to  $2.5$  and preferably from  $0.5$  to  $1.3$ , where for  $\text{H}_2\text{O}_2$  pure (100%) hydrogen peroxide is meant (any dilution water excluded). The molar ratios  $\text{NH}_3$ : ketone, carbonylic compound:  $\text{NH}_3$  and  $\text{NH}_3$ : $\text{H}_2\text{O}_2$  are preferably equal to or higher than 1 (even better higher than 1.5), otherwise parallel reactions can occur. The reaction medium may consist of water or of an organic solvent; tert-butanol and/or cyclohexanol, optionally in admixture with dioxane or toluene, proved to be really suitable solvents. The molar ratio solvent: carbonylic compound may generally range from  $0.1$  to  $100$ .

The following examples will illustrate the invention, without limiting however in any its scope.

Example 1

20 g of an (amorphous)  $\text{TiO}_2\text{-SiO}_2$  co-precipitate, traded by the GRACE Company as GRACE Silica-Titania No. 1 TYPE I, containing 2.6% by weight of Ti, having a surface area (BET) of  $467 \text{ m}^2/\text{g}$  and a pore volume of  $1.07 \text{ cm}^3/\text{g}$ , were dried at  $300^\circ \text{C}$  for 4 hours; thereafter they were dry-impregnated with  $20 \text{ cm}^3$  of an aqueous solution of tetrapropyl-ammonium hydroxide at 20% by weight. The thus impregnated solid material was directly transferred into a  $50 \text{ cm}^3$  autoclave, where the hydrothermal synthesis was carried out at  $150^\circ \text{C}$  in 10 days, without stirring. Then the solid product was rinsed with deionized  $\text{H}_2\text{O}$ , till neutral pH, dried at  $120^\circ \text{C}$  for 15 hours and calcined at  $430^\circ \text{C}$  for 10 hours. The molar ratio  $\text{Ti}:(\text{Ti} + \text{Si})$ , in the end product, was 0.0188, according to the elemental analysis, and 0.0183 according to the analysis by infrared ray (I.R.) spectrophotometry. The difference between the two values was not higher than the overall experimental error of the two methods. The volume of the intercrystalline cavities, measured by nitrogen absorption, was  $0.182 \text{ cm}^3/\text{g}$ , corresponding to a crystallinity degree higher than 95%. The average size of the obtained particles was 0.5 micrometers.

Example 2

A glass reactor, equipped with a stirrer and heating jacket, was pressurized with an inert gas (nitrogen). Then 1.5 g of a fine powder of titanium-silicalite, obtained according to example 1 were loaded into the reactor. One added then 21 g of water (1.17 moles), 25 g of t-butyl alcohol (0.34 moles) and 4 g of ammonia (0.24 moles); after having put the whole under stirring, 10.34 g of cyclohexanone (0.105 moles) were loaded, thereby forming a biphasic (solid-liquid) system, that was kept homogeneous by powerful stirring. Temperature was gradually increased up to  $80^\circ \text{C}$ , by conveying a thermostatic liquid into the reactor jacket. One started then to feed into the reactor, by means of a metering pump, an aqueous solution of hydrogen peroxide at 27.4% by weight. During the heating, the pressure rose slightly over the atmospheric level.

The addition of hydrogen peroxide was continued over 5 hours and 11.33 of  $\text{H}_2\text{O}_2$  (0.096 moles) were fed (on the whole); during the addition a pressure drop was registered.

After cooling, one added to the thus obtained suspension ethyl ether and one stirred for a few minutes; then the aqueous and ethereal phases were separated from the catalyst by filtration. The liquid phases were separated (in a separatory funnel) and the gaschromatographic analysis showed an 85.4% cyclohexanone conversion and a 95.9% selectivity to oxime; 6.4% of  $\text{H}_2\text{O}_2$  was lost because of decomposition and the oxime yield (with respect to  $\text{H}_2\text{O}_2$ ) was 90.0%.

Example 3 (Activating washing of the catalyst with  $\text{H}_2\text{O}_2$ )

10 g of the titanium-silicalite prepared according to example 1 were soaked (at  $70^\circ \text{C}$ ) into an aqueous solution, prepared by mixing under stirring  $20 \text{ cm}^3$  of aqueous  $\text{H}_2\text{O}_2$  (at 30% by weight) with  $177 \text{ cm}^3$  of aqueous of  $\text{H}_2\text{SO}_4$  at 10% by weight; after 2 hours the liquid was separated by decantation. This activating washing (with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ ) was repeated twice with a fresh solution, whereafter a filtration was carried out, followed by a long rinsing with deionized  $\text{H}_2\text{O}$  (till neutral pH). The rinsed solid was dried at  $120^\circ \text{C}$  for 15 hours and finally calcined in the air at  $550^\circ \text{C}$  for 2 hours. The molar ratio  $\text{Ti}:(\text{Ti} + \text{Si})$ , in the end product was 0.0167 according to the elemental analysis. The volume of the intercrystalline cavities, measured by nitrogen absorption, was  $0.183 \text{ cm}^3/\text{g}$ .

Example 4

Example 2 was repeated replacing the former catalyst by a new catalyst, activated by a treatment with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  as described in example 3; the experimental procedure was the same, whereas the amounts of the reactants were: 10.42 g of cyclohexanone (0.106 moles) and 11.67 g of  $\text{H}_2\text{O}_2$  at 2.4% (0.094 moles). One obtained the following results:

Cyclohexanone conversion	83.8%
Selectivity of cyclohexanone to oxime	99.7%
Oxime yield (with respect to H <sub>2</sub> O <sub>2</sub> )	94.4%
Hydrogen peroxide loss	2.5%

#### Example 5

Example 3 was repeated, replacing the basic co-precipitate by an amorphous co-precipitate traded by the GRACE Company as Silica-Titania No. 2 Type III, containing 1.38 by weight of titanium, having a surface area (BET) of 342m<sup>2</sup>/g and a pore volume of 1.21 cm<sup>3</sup>/g. The product obtained from the hydrothermal synthesis, activated by a treatment with H<sub>2</sub>SO<sub>4</sub> and hydrogen peroxide, showed a molar ratio Ti:(Ti+Si) of 0.0122 according to the elemental analysis. The volume of the intercrystalline cavities, measured by nitrogen absorption, was 0.184 cm<sup>3</sup>/g, corresponding to a crystallinity degree of 98%; the average size of the obtained particles was about 0.5 micrometers.

#### Example 6

Example 2 was reported replacing the former catalyst by a new catalyst prepared according to the procedure described in example 5 (starting from a different TiO<sub>2</sub>-SiO<sub>2</sub> matrix), activated, after the hydrothermal synthesis, by a treatment with H<sub>2</sub>SO<sub>4</sub> and hydrogen peroxide; the amount of the reactants were 9.51 g of cyclohexanone (0.097 moles) and 10.25 g of H<sub>2</sub>O<sub>2</sub> at 31.5% (0.095 moles). The obtained results were:

Cyclohexanone conversion	88.8%
Selectivity of cyclohexanone to oxime	100%
Oxime yield (with respect to H <sub>2</sub> O <sub>2</sub> )	91.7%
Hydrogen peroxide loss	7.5%

The results of the examples are summarized in Table 1.

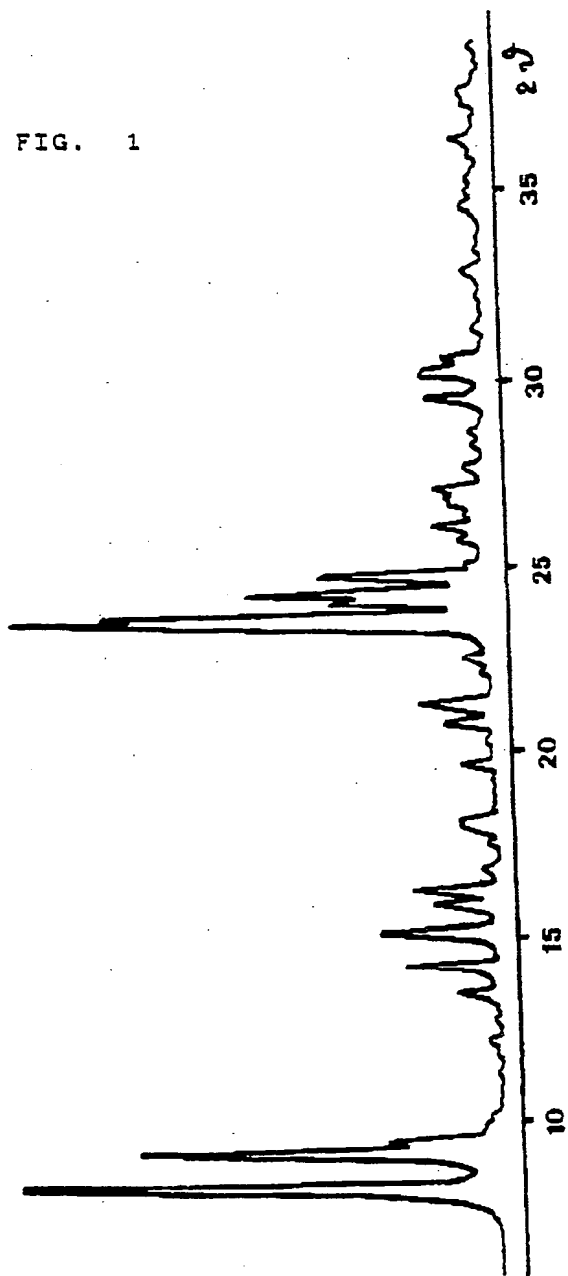
TABLE 1

EXAMPLE	2	4	6
Catalyst	From ex. 1	From ex. 3	From ex. 5
Ketone conversion (%)	85.4	83.8	88.8
Selectivity of ketone to oxime (%)	95.9	99.7	100
Oxime yield, with respect to H <sub>2</sub> O <sub>2</sub> (%)	90.0	94.4	91.7
H <sub>2</sub> O <sub>2</sub> loss (%)	6.4	2.5	7.5

#### Claims

1. A method for the preparation of titanium-silicalites in the presence of a templating agent, characterized in that a co-precipitated TiO<sub>2</sub>-SiO<sub>2</sub> material, amorphous or having a crystalline structure, containing titanium, silicon and oxygen in a combined form, is impregnated with an aqueous solution of said templating agent and in that the thus impregnated material is made to acquire the zeolitic structure of the titanium-silicalites by means of a hydrothermal synthesis.

2. A method according to claim 1, wherein said co-precipitated material is amorphous.
3. A method according to claim 1 or 2, wherein the pore volume of the co-precipitate is higher than 0.5 cm<sup>3</sup>/g, the surface area being higher than 200 m<sup>2</sup>/g.
4. A method according to anyone of the preceding claims, wherein the SiO<sub>2</sub>:TiO<sub>2</sub> molar ratio, in said co-precipitate, ranges from 20 to 200 and preferably from 30 to 80.
5. A method according to anyone of the preceding claims, wherein said co-precipitate is impregnated according to the dry-impregnation technology.
6. A method according to anyone of the preceding claims, wherein the titanium-silicalite undergoes, before being used, an activating washing, based on hydrogen peroxide, optionally in the presence of an inorganic acid.
7. A method according to anyone of the preceding claims, wherein said templating agent is selected from tetrapropyl-ammonium hydroxide and tetrapropylammonium bromide.
8. A method according to claim 7, characterized by the following molar ratios (in the material undergoing the hydrothermal synthesis):
  - 15 SiO<sub>2</sub>/TiO<sub>2</sub> = from 20 to 200
  - OH<sup>-</sup>/SiO<sub>2</sub> = from 0.03 to 0.20
  - H<sub>2</sub>O/SiO<sub>2</sub> = from 0.10 to 10
  - R<sub>4</sub>N<sup>+</sup>/SiO<sub>2</sub> = from 0.03 to 0.20
 wherein R<sub>4</sub>N<sup>+</sup> is the nitrogen containing organic cation corresponding to the templating agent used.
9. A method according to claim 8, characterized by the following ratio:
  - 20 SiO<sub>2</sub>/TiO<sub>2</sub> = from 30 to 80
  - OH<sup>-</sup>/SiO<sub>2</sub> = from 0.05 to 10
  - H<sub>2</sub>O/SiO<sub>2</sub> = from 0.50 to 4
  - R<sub>4</sub>N<sup>+</sup>/SiO<sub>2</sub> = from 0.05 to 0.10
10. Use of the product prepared according to the method described in anyone of the preceding claims, for the oxidation of propylene to propylene oxide.
11. Use of the product prepared according to the method described in anyone of the claims 1 to 9 for the ammoximation in the liquid phase of a carbonylic compound.
12. Use according to claim 11, wherein said carbonylic compound is cyclohexanone.
13. Use according to claim 12, wherein said cyclohexanone is fed to the ammoximation zone in the form of a mixture with cyclohexanol and hydrogen peroxide.
14. Use according to claim 13, wherein said mixture comes from a partial oxidation in the liquid phase (autooxidation) of cyclohexanol.
15. Titanium-silicalites, obtainable according to the method described in anyone of the claims form 1 to 9, consisting of particles having an average size ranging from 0.2 to 0.5 micrometers, in which the .Ti: (Ti + Si) molar ratio ranges from 0.0120 to 0.0190 and in which the volume of the intercrystalline cavities ranges from 0.170 to 0.185 cm<sup>3</sup>/g.
16. Titanium silicalites according to claim 15, showing the X ray diffractogram of figure 1 and/or the I.R. spectrum of figure 2.



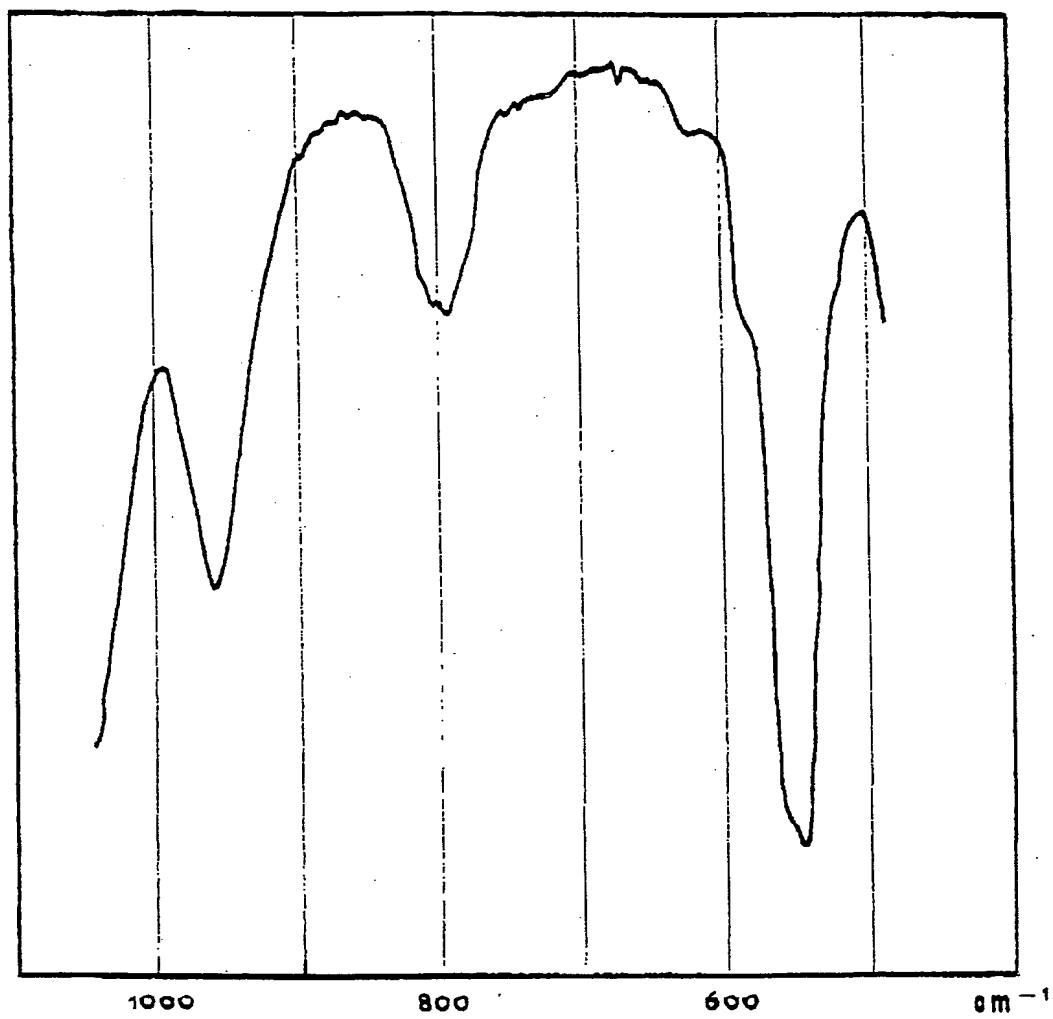


Fig. 2